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(54) Process for treating chromium platable polyacetals with an acid mixture.

(57) Chromium platable polyacetals are treated, in preparation for their subsequent metallization, by treatment with a mixture having the following composition :

Pure 96/98 % H <sub>2</sub> SO <sub>4</sub>	= 30 %
Pure 80 % H <sub>3</sub> PO <sub>4</sub>	= 20 %
Pure 35/36 % HCl	= 5 %
H <sub>2</sub> O	= 45 %

The present invention relates to molded articles having a partially metallized free (open) surface for decorative or technical purposes. It also relates to a process for obtaining such parts from a composite material.

Plastic parts presenting metallized surface areas on exactly defined zones, called selective surface areas, may be required for decorative parts that are intended for applications in perfumery, cosmetics, automobiles, health articles, etc. They may also be required for any application making use of the electrical conductivity of metals and insulation properties of plastics.

One of the known metallization processes for plastics which gives good results has been proposed by the Shipley Company under the name of the Shipley P.O.P process. In this process, which can be performed continuously, metallization of the plastic materials is performed by electrolysis in an aqueous phase, after chemical conditioning of the whole surface.

When it is desired to obtain a selective metallization of certain surfaces, it is necessary to cover the areas which are not to be metallized with a mechanical protection coating, then to remove this protection after the metallization process in order to obtain the partially metallized part.

This process is not satisfactory because parts which comprise only a single material can only be obtained by a succession of delicate handling operations, thereby losing the benefit of a continuous production process without a change in equipment.

Accordingly, the object of the present invention is to obtain a molded article having a partially metallized free (open) surface, characterized in that it is obtained by first molding a plastic material, then over-molding with a second plastic material, only of the aforesaid plastic materials being chemically metallizable by a wet process.

Such a part can for example be used to produce stoppers or decorative bottles, plates for the dashboards of automobiles, the front part of electronic materials or of any furniture where it is desired to obtain both plastic and metal appearances.

It can also be used for any application where it is desired to obtain selective conduction of electricity by a metal, while the plastics behave as insulators.

Alternatively it is possible to first mold the metallizable plastic material, or to start by molding the non-metallizable plastic material. In practice, the first material molded is the one present in greater proportion and intended to ensure the structure of the final part.

According to one characteristic of this invention, the molded article having a partially metallized free (open) surface comprises a plastic material which is chemically metallizable by a wet process, selected from the group of thermoplastic materials, particularly including the following materials: ABS, chromium platable polypropylene, ABS/polycarbonate, polyphenylene oxide, chromium platable polyacetal.

It is possible to use thermoplastic materials of the Terluran® type, which is an ABS in the form of a granulate produced by BASF Company, or Novodur®, which is an ABS produced by BAYER FRANCE. The polyacetal can for example be of the Kematal® type, which is an acetal in the form of resins produced by the AMCEL Company. It is also possible to use Ultraform®, of a chromium platable type, which is a polyoxy methylene in the form of a granulate produced by the BASF Company.

According to another characteristic of this invention, the molded article having a partially metallized free (open) surface comprises a plastic material which is chemically metallizable by a wet process, selected from among the group of thermally hardenable (thermosetting) materials, particularly including the following materials: phenolic resin, urea formaldehyde, melamine, polyester.

The metallizable thermoplastic or thermosetting materials have in common similar properties for obtaining hydrophilic microporous surfaces. The creation of such surfaces is one of the key steps of the

chemical metallization process by a wet method and for obtaining selective surfaces. These microporous surfaces are obtained by oxidation or chemical dissolution in mediums for specific chemical attack. The chemically non-metallizable plastics will resist this kind of attack.

The present invention preferably relates to a molded article having a partially metallized free (open) surface, comprising a plastic material which is chemically metallizable by a wet process and a plastic material which is not chemically metallizable by a wet process, selected from among the group including the following materials: polyethylene, polystyrene, polypropylene, polyesters of P.E.T.G-P.C.T.G type, polycarbonate, polymethyl methacrylate, polyamide, SAN, PTFE.

A molded article having a partially metallized free (open) surface can moreover be characterized in that the metallized surface comprises a base metal selected from among copper or nickel deposited by chemical means.

The resulting metallized surface can be covered with a second metal film, which is constituted from a metal, in particular one selected from among the following metals: copper, nickel, chromium, gold, platinum palladium, rhodium, ruthenium, silver, zinc, cobalt, or an alloy based on the above mentioned metals.

Almost any metal deposit can be produced, the choice depending on the desired final appearance. For example, copper gives a glossy or semi-glossy finish, nickel, a glossy, matte or velvety finish.

The present invention also has as its objective to provide a process for obtaining a molded article having a partially metallized free (open) surface, characterized in that :

- a) a first plastic material is first molded by injection or compression in a first mold,
- b) a second, different plastic material is molded by injection or compression in a second mold onto the intermediate part obtained above in order to create a surface decoration on the final part,
- c) the resulting composite material is demolded,
- d) the surface of one of the two plastic materials is selectively conditioned by creating a hydrophilic microporous surface via oxidation or chemical dissolution,
- e) catalyst particles are deposited on the hydrophilic microporous surface,
- f) the hydrophilic microporous surface is selectively chemically metallized using a wet process.

The process thus consists in performing two complementary and distinct molded shapes (articles).

For example, the first non-metallizable material is molded by injection or compression into the first mold. The mold is rotated and this is followed by molding the second metallizable material by injection or compression into the second mold.

The steps can be reversed, such that, for example, the metallizable material is molded first and the non-metallizable material second.

The quality of the molding is one of the primary factors for good metallization of the plastic material. Thus, certain standards must be respected: for example, release agents must not be used.

The microporous surfaces obtained by oxidation or chemical dissolution allow formation of catalytic sites leading to chemical deposition of copper or nickel.

The copper or nickel deposits can be strongly anchored in these pores, which are activated by catalysis, and this makes it possible to obtain high adhesion values of the resulting metal deposits.

The quality of the definition between the microporous surface which is metallizable after chemical treatment and the non-metallizable surface is defined by the value of the angle alpha ( $\alpha$ ) at the solid/liquid interface. It is understood that the parameters which control the wetting properties of the metallizable

material and the hydrophobicity of the non-metallizable material are controlled by adjusting the chemical treatment media.

A metallization accelerator is preferably applied to the microporous surface, after step e) and before step f).

This accelerator, for example PM 964® sold commercially by the Shipley Company, accelerates the initial metal deposition, protects the metallization bath against catalyst entrainment, prevents metallization of the equipment. The accelerator PM 964 of the Shipley process was developed specifically for the metallization of ABS and has properties especially adapted for polypropylene.

According to one of the characteristics of this invention, the catalyst of step e) is constituted from palladium or tin colloids which are deposited into the pores of the aforementioned surfaces, which are thus activated.

This catalyst deposits palladium or tin particles onto the surface which are necessary for the subsequent bonding of the metal. This catalysis must be absolutely uniform to produce a shiny mirror which is free of punctures and granularity.

The present invention relates to a process for obtaining a molded article having a partially metallized free (open) surface as defined above, is characterized in that a second metal finishing film is deposited onto the chemically metallized surface.

In one embodiment of the process for producing a molded article having a partially metallized free (open) surface, after demolding the part made from composite material, a wet metallization process is performed with the following range of thermoplastic and thermosetting materials (for example P.O.P Shipley), said process comprising the following steps:

- 1 - Cleaning and wetting the surfaces with for example PM 90® Cleaner at a concentration of 1.25 l of PM 90® Cleaner per 100 l of bath.  
Purpose: solution of a specific surfactant for the different plastics, which cleans the surface and uniformizes the action of the conditioner before the chemical attack.  
This product is allowed to act for 1 to 5 min at 50-60°C.
- 2 - Rinsing, can be performed with water.
- 3 - Sulfo-chromic treatment with for example ETCH PM 940® sold commercially by Shipley. The following are used per 100 l of bath :  
36 kg of chromic acid.  
60 l of deionized water,  
20 l of sulfuric acid (1.84),  
10 l of ETCH PM 940®.  
This conditioning is performed at 60-65°C for 3 to 10 min, and confers good adhesion of the metal coating to the plastic material. This is in fact a sulfuric/chromic acid mixture in an aqueous medium which is used to oxidize butadiene in styrene-containing materials (creation of pores) or to dissolve mineral inclusions (creation of pores).
- 4 - Rinsing: 3X rinsing with water, the last rinse must be colorless.
- 5 - Neutralization with for example bath PM 955® sold commercially by Shipley, at 35°C for 1 min. The following are used per 100 l of bath :  
6 kg of PM 955® Neutralizer  
10 l of hydrochloric acid, and the complement of water.  
This bath causes the chemical reduction of hexavalent chromium into inert trivalent chromium in the bottom and on the surface of the etched regions.
- 6 - Rinsing: 2X rinsing with deionized water.
- 7 - Preconditioning for the catalysis by immersion in an HCl reagent. This bath is prepared with 75 l of deionized water per 25 l of HCl. The surfaces are thus prepared at ambient temperature for 2 to 3 min by applying a highly polar layer of HCl.

- 8 - Covering with palladium/tin colloid, for example Catalyst 9 F® sold commercially by Shipley, at ambient temperature for 2 to 3 min. This catalyst comprises per 100 l of bath :  
62.5 l of deionized water,  
25 l of pure hydrochloric acid,  
12.5 l of concentrated Catalyst 9 F®.

The palladium concentration is maintained between 80 and 100 % by adding the Catalyst 9 F® and the bath level is maintained by adding concentrated hydrochloric acid or water depending on the acidity of the solution.

In this step, the treated surfaces and the pores are covered with highly catalytic palladium-tin colloid, in preparation for the subsequent deposition.

- 9 - Rinsing: 2X with deionized water.
- 10 - Acceleration - reduction, for example with the accelerator PM 964® sold commercially by Shipley, for 3 min, at 35-40°C.  
6 kg of accelerator PM 964® and 2.5 l of concentrated sulfuric acid are used for 100 l of accelerator PM 964® bath

This eliminates the tin in order to enhance the catalytic activity of palladium.

- 11- Rinsing: 2X with deionized water.
- 12- Nickel deposition by chemical reduction in a reducing alkaline medium, with for example chemical nickel PM 980® sold commercially by Shipley, for 5 to 7 min., at 24-35°C.  
This bath consists of strongly complexed nickel salts in an alkaline medium, in the presence of a reducing agent. This type of chemical bath for nickel is also available in an acid medium.  
The following are used per 100 l of bath :  
84 l of deionized water,  
14 l of PM 980®,  
2.4 l of ammonia.

The nickel concentration is maintained between 70 and 100 % by adding PM 980® and PM 980<sup>(s)</sup>. The bath pH must be periodically adjusted to 8.5-9.5 with ammonia.

Alternatively, it is possible to substitute the chemical deposition of nickel in step 12 with the chemical deposition of copper in order to obtain a copper deposit by chemical reduction in an alkaline medium.

The bath then consists of strongly complexed copper salts in an alkaline medium in the presence of a powerful reducing agent. For example, it is possible to use Cuposit 251® stabilized with the EDTA, which makes it possible to obtain a thick copper deposit having a fine-grained structure, capable of improving the masking processes. This type of bath is not available in an acid medium.

For purposes of treating chromium platable polyacetals, the following specific sequence is used :  
Steps 1 and 2 are identical to the steps described above.

In step 3, the chemical etching bath is as follows

Pure 96/98 % H <sub>2</sub> SO <sub>4</sub>	= 30 %
Pure 85 % H <sub>3</sub> PO <sub>4</sub>	= 20 %
Pure 35/36 % HCl	= 5 %
H <sub>2</sub> O	= 45 %

Under the following conditions :

Duration of treatment: 4 to 12 min

Temperature : 26 to 35°C

Density of the bath at 20°C: 1.45 – 1.47.

- 4 - Rinsing with water
- 5 - Neutralizing rinse with 5 % NaOH + anionic wetting agent
- 6 - Rinsing
- 7 - HCl immersion
- 8 - Catalyst 9 F®
- 9 - Rinsing
- 10 - Accelerator PM 964
- 11 - Rinsing
- 12 - Chemical nickel PM 980 deposition  
or

### 13 -Chemical copper deposition.

## CLAIMS

1. Process for treating chromium platable polyacetals in preparation for their metallization, consisting of surface treatment with a mixture of acids selected from among the group of sulfuric, phosphoric and hydrochloric acids, characterized in that the mixture has the following composition:

pure 96/98% $\text{H}_2\text{SO}_4$	= 30%
pure 80% $\text{H}_3\text{PO}_4$	= 20%
pure 35/36% $\text{HCl}$	= 5%
$\text{H}_2\text{O}$	= 45%

2. Process according to claim 1, characterized in that said treatment lasts for 4 to 12 minutes.

3. Process according to any of the claims 1 to 2, characterized in that the density of the mixture is comprised between 1.45 and 1.47.

4. Process according to any of the claims 1 to 3, characterized in that the treatment is followed by chemical deposition of a base metal selected from among copper or nickel.

5. Process according to claim 4, characterized in that the resulting metallized surface is covered with a second metal film, in particular a metal chosen from among the following metals: copper, nickel, chromium, gold, platinum, palladium, rhodium, ruthenium, silver, zinc, cobalt, or an alloy based on the above-mentioned metals.

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a molded article having a partially metallized free (open) surface, comprising a plastic material which is chemically metallizable by a wet process